

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C12P 7/62, C08J 3/12 // C08L 67:04	A1	(11) International Publication Number: WO 94/02622 (43) International Publication Date: 3 February 1994 (03.02.94)
(21) International Application Number: PCT/GB93/01465 (22) International Filing Date: 13 July 1993 (13.07.93) (30) Priority data: 9215791.6 24 July 1992 (24.07.92) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; Imperial Chemical House, 9 Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : LIDDELL, John, MacDonald [GB/GB]; 678 Yarm Road, Stockton-on-Tees, Cleveland TS16 0DP (GB). GEORGE, Neil [GB/GB]; 10 Westward Lane, Ingleby Barwick, Stockton-on-Tees, Cleveland TS17 0UY (GB).		(74) Agents: LOCKE, Timothy, John et al.; Group Patent Services Department, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS OF INCREASING THE PARTICLE SIZE OF POLYMERS (57) Abstract Polyester particles in suspension in a liquid can be agglomerated below their melting points and the agglomerated particles are more easily filtered.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

PROCESS OF INCREASING THE PARTICLE SIZE OF POLYMERS

In the production of polyester polymers especially those which are microbially produced the particle sizes of the polymers may be too small for convenient handling; for example in the course of production processes it may be necessary to separate such particles from aqueous liquid media. Such separations are more difficult if the particles are small than if they are large.

Surprisingly we have found that polyesters, especially those which are microbially produced, for example polymers and copolymers of hydroxyalkanoic acids especially polymers and copolymers of hydroxybutyric acid are capable of surprisingly rapid agglomeration at temperatures substantially below their peak melting points when in suspension in a liquid medium producing particles well suited to solid liquid separation with little molecular weight loss.

This invention comprises a process in which polyester particles, in suspension in a liquid medium in which if such medium comprises matter derived from microbial cells the said matter other than polyester has been at least partly chemically degraded, are agglomerated by maintaining the suspension at a temperature in excess of 80°C and preferably in excess of 90°C for example in excess of 100°C and preferably 30 to 80°C and more preferably 40 to 70°C below the peak melting point of the polyester as determined by differential scanning calorimetry for a time sufficient to cause substantial agglomeration.

Suitable temperatures in the case of polymers of hydroxybutyric acid, for example copolymers of hydroxybutyric and hydroxyvaleric acid containing up to 25%, for example 5 to 20% of hydroxyvaleric acid residues, the balance being substantially all hydroxybutyric acid residues, are in the range 120 to 160°C. In general a considerable amount of agglomeration can be achieved with such materials in about

1 minute at 130°C. The large particles formed are agglomerates of the fine particles of the original suspension. The fine particles, in the case of microbially produced polymers, are usually <1µm in diameter (as assessed by the diameter of a sphere of equivalent volume). The process in this case, especially in the case of polymers of hydroxybutyric acid and copolymers thereof with hydroxyvaleric acid, enables the production of a fused network of polymer strands resulting in a highly porous, mechanically strong agglomerate with excellent filtration and washing characteristics. Suitably, the agglomerates produced have a weight average diameter of at least 50µm and preferably 100 to 1000 µm, for example 200 to 500µm. They suitably have a high porosity for example 0.7 to 0.8 and preferably at least 0.6. Relative to non-agglomerated particles the filtration rate (based on the specific cake resistance) is increased by 100 to 10,000 times. Agglomeration may be achieved with minimal influence on molecular weight. At 30 minutes residence time at 130°C <30% reduction is obtained, and at 1 minute the loss is undetectable.

It will be appreciated that it is necessary where the particles are derived from microbially produced polyester that the residual microbial material surrounding the particles should be at least sufficiently degraded to permit the polyester particles to come into contact with one another in the liquid medium.

We have surprisingly found that an increase in particle sizes may still be obtained despite the presence of soluble microbial components and degradation products. It may be desirable, especially if the particles initially recovered are contaminated with microbial matter or degradation products thereof to resuspend them in a second liquid medium and/or further treat them for example with a second liquid medium in which further processing for example chemical treatment (which may be treatment with a bleach for example hydrogen peroxide)

may take place and to recover the particles from the new liquid medium. The process of increasing the particle size may take place at any point in the process. Such a step could take place in the presence of a liquid medium which is substantially free from contaminants and which contains substantially only materials which are desired in the final polymer or which are readily separable therefrom with the liquid.

The particle sizes are suitably increased by agitation for example in turbulent flow such as a heated stirred tank pressure vessel at a temperature at least 30°C and more preferably at least 40°C and preferably at most 80°C and more preferably at most 70°C below the melting point of the polyester as determined by the peak melting point as determined by differential thermal scanning calorimetry.

The process may be carried out by the direct injection of steam at a suitable temperature and pressure into a flowing stream of the suspension. This has the advantage that the suspension can be agglomerated continuously. However, it is surprisingly found to be possible to carry out the process in the presence of moving parts for example stirrers.

The liquid medium preferably comprises water as this is cheap and non-polluting and is very effective.

We have found that the process may be carried out with a solids concentration of up to 200 grams per litre and preferably 40 to 130 grams per litre. Above these levels there is a tendency for the medium to become substantially immobile because of the inclusion of liquid within the porous structure of the solid. The ability of the particle to be washed free from soluble cellular material is not unduly impaired by the agglomeration process.

**EXAMPLE 1 : Agglomeration of polyhydroxybutyrate/
polyhydroxyvalerate copolymer suspensions by
thermal treatment.**

A suspension of polyhydroxybutyrate/valerate polymer (8%
5 molar hydroxyvalerate, 92% hydroxybutyrate) in water derived
from *Alcaligenes eutrophus* and containing about 2% of cellular
matter derived therefrom as an impurity was agglomerated by
heating to 130°C for 30 minutes in a stirred tank reactor. The
resulting agglomerated suspension was filtered through a GFC
10 cellulose filter (nominal pore size 1.5 micron) in a pressure
filter at about 2.5×10^4 pascals pressure.

Comparative filtration data is shown for the suspension
before and after the thermal agglomeration treatment in Table 1
together with data on the particle size and colour of the
15 washed melt processed polymer.

TABLE 1	Weight Average Size ⁽¹⁾ (micron)	Relative Filtration Rate ⁽²⁾	Polymer Yellowness ⁽³⁾ (D1925-70 yellowness units)	Weight Av mol weight (K)
---------	--	---	---	-----------------------------------

Before thermal agglomeration	72	1	47 (±5)	377
After thermal agglomeration (130°C, 30 minutes)	346	1000	46 (±5)	302

- (1) As determined by a Malvern laser sizer
- (2) The relative filtration rate is based on specific cake
resistance.
- 30 (3) Centrifuged, washed by resuspension and re centrifugated
in the non-agglomerated case. Filtered and washed on the
filter bed only in the agglomerated case.

EXAMPLE 2 : Agglomeration in the presence of high concentrations of cellular debris

A suspension of PHB/V (copolymer of hydroxybutyric and hydroxyvaleric acid) (12% molar hydroxyvalerate, 88% hydroxybutyrate) in water derived from *Alkaligenes eutrophus* containing 5% soluble matter derived therefrom as an impurity, was agglomerated by heating for 2 minutes in a stirred tank reactor at 126°C. The resulting agglomerated suspension was filtered through a 50µm filter cloth in a pressure filter at 7000 Pa. The suspension was washed and analysed as above.

TABLE 2	Weight Average Size ⁽¹⁾ (micron)	Relative Filtration Rate ⁽²⁾	Polymer Yellowness ⁽³⁾ (D1925.70 yellowness units)
---------	--	---	--

Before thermal agglomeration	1.0	1	45
After thermal agglomeration	300	2500	54

EXAMPLE 3 : Continuous Thermal Agglomeration by Direct Steam Injection

A suspension of PHB/V (8% hydroxyvalerate) in water derived from *Alcaligenes Eutrophus* containing 0.13% w/w soluble matter derived therefrom as an impurity, was continuously thermally agglomerated within a flowing suspension by direct steam injection. The temperature was set at 125°C, the residence time was 1 minute and turbulent conditions were maintained to achieve the following characteristics.

6

TABLE 3

TABLE 3	Weight	Relative	Polymer	Weight Av	
	Average	Filtration	Yellowness	mol	
	Size ⁽¹⁾	Rate ⁽²⁾	⁽³⁾	weight	
	(micron)		(D1925-70	(K)	
5			yellowness		
			units)		
	Before thermal				
	agglomeration	21.4	1	41	523
	After thermal				
10	agglomeration	250	2500	34	578

It will be seen that an important process improvement is obtained and the yellowness test indicates the substantially complete removal of impurities in all cases. If desired, the polymer may be re-suspended and filtered or the filter bed may be further washed to remove further cellular matter if desired. Less intensive solid/liquid separation techniques for example pressure filtration, decanter centrifuges produced results comparable to high g force centrifugal separation on non-agglomerated particles.

Each polymer sample was dried and melt processed at 170°C for 4 minutes and the polymer colour measured in terms of yellowness index to ASTM D1925-70. No detrimental effect of polymer colour was apparent comparing the technique of washing and centrifugation with the approach of thermal agglomeration, filtration and washing.

CLAIMS

SBI37088

- 1 A process in which polyester particles in suspension in a liquid medium in which if such medium comprises matter derived from microbial cells the said matter other than polyester has been at least partly chemically degraded are agglomerated by maintaining the suspension at a temperature in excess of 80°C and preferably in excess of 90°C for example in excess of 100°C and preferably 30 to 80°C and more preferably 40 to 70°C below the peak melting point of the polyester as determined by differential scanning calorimetry for a time sufficient to cause substantial agglomeration.
- 2 A process as claimed in Claim 1 in which the polyester is microbially produced.
- 3 A process as claimed in Claim 1 or 2 in which the polyester is a copolymer of hydroxybutyric acid and hydroxyvaleric acid containing up to 25% of hydroxy-valeric acid residues, the balance being substantially all hydroxybutyric acid residues.
- 4 A process as claimed in Claim 3 which is carried out at a temperature of 120 to 160°C.
- 5 A process as claimed in any preceding claim in which particles of which substantially all are smaller in diameter than 1µm are agglomerated to produce agglomerates of weight average diameter of at least 50µm.
- 6 A process as claimed in any preceding claim in which the aggregates have a porosity greater than 0.7.
- 7 A process as claimed in any preceding claim which is carried out under turbulent conditions.
- 8 A process as claimed in Claim 7 in which the process is carried out by direct injection of steam into a flowing stream of the suspension or whilst stirring.
- 9 A process as claimed in any preceding claim in which the liquid medium comprises water.
- 10 A process as claimed in any preceding claim in which the

agglomerated particles are separated from the liquid medium by filtration.

11 A process as claimed in Claim 10 in which the separated agglomerated particles are further washed optionally by resuspending them in a medium comprising water and/or chemically treated optionally while resuspended, and the particles are recovered.

INTERNATIONAL SEARCH REPORT

Internat. Application No.
PCT/GB 93/01465

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C12P7/62 C08J3/12 //C08L67:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08J C08G C12P C12N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 479 043 (PCD POLYMERE GESELLSCHAFT M.B.H.) 8 April 1992 see claims 1,2,8,9 see page 2, column 1, line 15 - line 22 see page 3, column 4, line 42 - line 52	1-3,7, 9-11
A	EP,A,0 046 335 (IMPERIAL CHEMICAL INDUSTRIES PLC) 24 February 1982 see claims 1,4,9 see page 1, line 4 - line 7 see page 3, line 22 - line 30	1,2,9,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

4 November 1993

Date of mailing of the international search report

15. 11. 93

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

NIAOUNAKIS, M

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 93/01465

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0479043	08-04-92	AT-B- 395319 JP-A- 4264125 US-A- 5213976	25-11-92 18-09-92 25-05-93
EP-A-0046335	24-02-82	JP-A- 57174094	26-10-82